



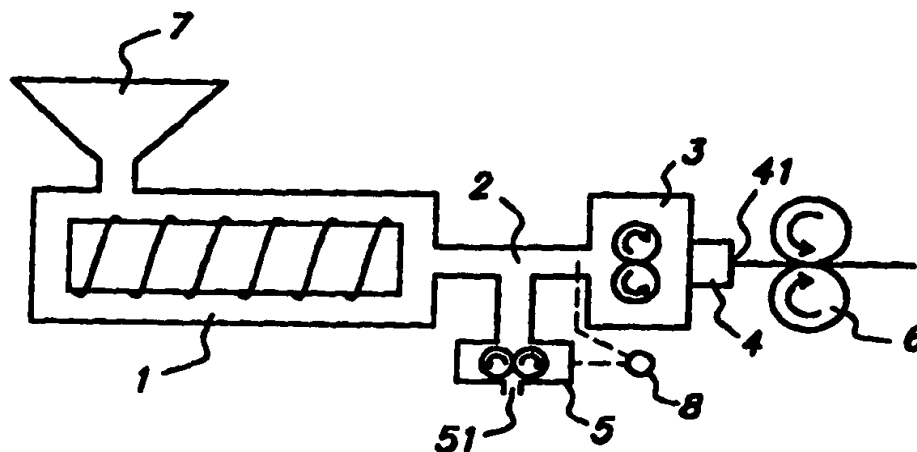
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>B29C 47/92, 47/50</b>		A1	(11) International Publication Number: <b>WO 99/03666</b>
			(43) International Publication Date: 28 January 1999 (28.01.99)
(21) International Application Number: PCT/US98/14159		(81) Designated States: AU, CN, IL, JP, KR, MX, RU, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 10 July 1998 (10.07.98)			
(30) Priority Data: 08/891,757 14 July 1997 (14.07.97) US		Published With international search report.	
(71) Applicant: RAYCHEM CORPORATION [US/US]; 300 Constitution Drive, Mail Stop 120/1A, Menlo Park, CA 94025-1164 (US).			
(72) Inventors: CHU, Edward, F.; 1714 Banff Drive, Sunnyvale, CA 94087 (US). JORDAN, Susan, M.; 3397 Ivan Way, Mountain View, CA 94040 (US). LAHLOUH, John; 674 Apache Court, San Jose, CA 95123 (US).			
(74) Agents: RICHARDSON, Timothy, H., P. et al.; Raychem Corporation, Intellectual Property Law Dept., 300 Constitution Drive, Mail Stop 120/1A, Menlo Park, CA 94025-1164 (US).			

(54) Title: EXTRUSION OF POLYMERS

## (57) Abstract

Processes and apparatus for melt extrusion of polymeric compositions, particularly conductive polymers, in which a gear pump (3) delivers molten polymeric composition to an extrusion orifice (41). Overfeeding of the composition due to pressure variations is avoided by means of a polymer relief means (5), preferably a second, smaller gear pump (5), which removes a portion of the molten composition when the pressure exceeds a selected level.



**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

-1-

## EXTRUSION OF POLYMERS

This invention relates to apparatus and methods for extruding polymer compositions.

5

Polymeric compositions are often shaped by melt extrusion. A conveying means conveys the molten polymeric composition as a continuous stream under pressure to an extrusion orifice, and forces it through the orifice to form an extrudate of desired shape. In many cases, the composition is fed as a solid to a conveying means which melts the composition through a combination of shearing and external heating. Well known conveying means include single screw and twin screw extruders. Unfortunately, conventional conveying means often fail to deliver the molten composition to the extrusion orifice at a constant rate, as a result of pressure variations within the conveying means, particularly when the composition has high viscosity. This results in an extrudate of variable quality. It is well known to mitigate this problem by placing a gear pump (alternatively known as a melt pump) between the conveying means and the extrusion orifice. The gear pump helps to deliver a substantially constant volume of molten polymeric composition to the extrusion orifice, and in consequence to produce an extrudate of improved quality. However, the gear pump must be correctly sized and the pressure variations must be small enough to ensure that the gear pump is neither starved nor overfed.

We have found that the problems outlined above are particularly serious when conductive polymers are melt extruded. The term "conductive polymer" is used herein to denote a composition which comprises a polymeric component and, dispersed therein, a particulate conductive filler, e.g. carbon black, graphite, a metal, a conductive ceramic, or a metal carbide or nitride. Particularly when the conductive polymer contains a high concentration of particulate filler (which may be only the conductive filler or a mixture of conductive and non-conductive fillers), pressure variations during the extrusion process can cause undesirable variation in the electrical properties of the extrudate, even when a gear pump is placed between the conveying means and the extrusion orifice.

We have discovered, in accordance with the present invention, that when a gear pump is used in combination with a conveying means and an extrusion orifice (as outlined above) greatly improved results can be obtained through the use of a polymer relief means, which, when the pressure in the gear pump exceeds a selected level,

-2-

bleeds molten polymer from the system, and thus ensures that the gear pump is not overfed (and, therefore, continues to deliver a constant volume of molten polymeric composition to the extrusion orifice).

5           The present invention is particularly suitable for use in the extrusion of conductive polymers and will be chiefly described by reference to such use. However, it is to be understood that the invention can also be used in the extrusion of other polymeric compositions, and that the information given herein for conductive polymers is applicable to other polymeric compositions (with, if appropriate,  
10       modifications which will be apparent to those skilled in the extrusion of polymers having regard to their own knowledge and the information herein).

          In one preferred aspect, the present invention provides a apparatus for producing a melt-extruded article composed of a polymeric composition, preferably a conductive  
15       polymer, the apparatus comprising

- (1) conveying means for conveying a molten polymeric composition under pressure;
- (2) a passageway;
- (3) a gear pump;
- 20       (4) an extrusion orifice; and
- (5) a polymer relief means

          the components (1), (2), (3) and (4) being arranged so that molten polymeric composition conveyed by the conveying means passes in a continuous stream sequentially through the conveying means, the passageway, the first gear pump and  
25       the extrusion orifice; and

          the polymer relief means being associated with the first gear pump so that, if the pressure in the first gear pump exceeds a first selected level, the polymer relief means removes molten polymeric composition from the continuous stream thereof until the  
30       pressure in the first gear pump falls below a second selected level. The second selected level is equal to or lower than the first selected level, and is sufficiently high to ensure that the removal of the molten polymeric composition does not reduce the pressure to a level which results in the melt pump being starved.

35           As discussed below, the polymer relief means is preferably a gear pump, and for this reason the gear pump (3) is often referred to herein as the "first" gear pump,

even though it is the only gear pump when the polymer relief means is a component other than a gear pump.

5 In a second preferred aspect, the present invention provides a method of making an article composed of a molten polymeric composition, preferably a conductive polymer, the method comprising the steps of

- (A) conveying a continuous stream of a molten polymeric composition under pressure to a gear pump;
- (B) operating the gear pump so that the molten polymeric composition  
10 conveyed to the gear pump in step (A) passes through the gear pump to an extrusion orifice and is extruded through the orifice; and
- (C) when the pressure within the gear pump exceeds a selected level, removing molten polymeric composition from the continuous stream thereof.

15 This invention is particularly useful when (a) the molten polymeric composition is of high viscosity (since this tends to increase the pressure variations in the extruder or other conveying means); and/or (b) the product is adversely affected by pressure variations during the extrusion process, e.g. if it has at least one dimension which is very small, or if it has electrical or other properties which are  
20 dependent on the shear which has been exerted on the composition during extrusion; and/or (c) the extruder (or other conveying means) is of a type which inherently tends to produce pressure variations. Thus, preferred processes of the invention have one or more of the following features:--

- (a) The polymeric composition
  - 25 (i) comprises a polymer having a melting point  $T_m$  °C;
  - (ii) has a viscosity of 2 to 15 K.Pa.sec., particularly 8 to 11 K.Pa.sec., at a shear rate of 50 sec<sup>-1</sup> at a temperature of 1.5 times  $T_m$ ; and
  - (iii) is extruded at a temperature of not more than 1.5 times  $T_m$ .

30 Such a composition can contain, for example, at least 35% by volume of one or more particulate fillers, preferably at least 40% by volume of a conductive filler, e.g. carbon black.

- (b)(i) The polymeric composition is a conductive polymer exhibiting PTC behavior, particularly such a composition having a resistivity less than 10 ohm-cm, particularly less than 1 ohm-cm.
- 35 (b)(ii) The polymeric composition is extruded as a sheet having a thickness less than 0.010 inch (0.25 mm), e.g. 0.005 inch (0.13 mm) or less; or is

-4-

extruded as a strand or sheet which has a thickness greater than 0.010 inch (0.25 mm) and is then calendered to a sheet having a thickness less than 0.010 inch (0.25 mm), e.g. 0.005 inch (0.13 mm).

- 5 (c) The polymer conveying means is (i) a reciprocating single screw extruder, or (ii) a non-reciprocating screw extruder having a relatively short length to diameter (l/d) ratio, e.g. less than 15:1, for example 8:1 to 15:1.

As noted above, the polymer relief means is preferably a second gear pump, but it can be any component which will permit the polymeric composition to escape from the system when the pressure becomes excessive and will prevent it from doing so when the pressure has dropped to the desired level. Suitable components include gear pumps, pressure relief valves, and suitable reclosable orifices. When, as is preferred, a second gear pump is used as the polymer relief means, it can be substantially smaller than the first gear pump. Thus, it is preferred that the ratio of the maximum capacity of the first gear pump to the maximum capacity of the second gear pump is 5:1 to 50:1, e.g. 15:1 to 25:1. Preferably, the operation of the second gear pump (or other polymer relief means) is controlled by a control system which continuously monitors the pressure exerted on the polymeric composition and operates the second gear pump in response to that pressure. The control system can monitor the pressure in the first gear pump directly or it can monitor pressure at some other part of the system where the pressure is representative of the pressure in the first gear pump, e.g. in the passageway between the conveying means and the first gear pump.

25 In order for the first gear pump to deliver a constant volume of molten polymeric composition to the extrusion orifice, the pressure within the gear pump should be between a lower value,  $P_{\text{lower}}$ , and an upper value,  $P_{\text{upper}}$ . The first selected level,  $P_1$  (above which the polymer relief means removes molten polymer), should be less than  $P_{\text{upper}}$ , preferably 0.25 to 0.9 times  $P_{\text{upper}}$ . The second selected level,  $P_2$  (below which the polymer relief means does not remove molten polymer) is (a) equal to or less than  $P_1$ , preferably from 0.4 to 1.0 times  $P_1$ , and (b) greater than  $P_{\text{lower}}$ , preferably 1.2 to 1.6 times  $P_{\text{lower}}$ . One of the advantages of the present invention is that because the polymer relief means ensures that pressure peaks in the extruder are not transmitted to the extrusion orifice, it is possible to operate at higher rates of extrusion than would be possible if the pressure peaks had to be below  $P_{\text{upper}}$  for the first gear pump.

This invention is particularly suitable for melt extruding conductive polymers of the kind used in circuit protection devices, i.e. PTC compositions which comprise a crystalline polymer, e.g. polyethylene or polyvinylidene fluoride, and a conductive  
5 particulate filler, preferably carbon black, in amount sufficient to reduce the room temperature resistivity to a low level, e.g. less than 5 ohm-cm.

Suitable conductive polymer compositions are disclosed in U.S. Patent Nos. 4,237,441, 4,388,607, 4,534,889, 4,545,926, 4,560,498, 4,591,700, 4,724,417,  
10 4,774,024, 4,935,156, 5,049,850, and 5,250,228, 5,378,407, 5,451,919, 5,582,770 and 5,747,147 and International Publication No. WO 96/29711.

The conductive polymer can be fed to the conveying means in any appropriate way, including  
15 (a) in the form of a solid, e.g. pellets, prepared by a previous melt mixing process in which the conductive filler is dispersed in the polymer component; or  
(b) in the form of a dry blend of the polymeric component and the conductive filler, in which case the conveying means must be one which will melt-mix  
20 these ingredients, as well as convey them to the first gear pump; or  
(c) in the form of a molten dispersion of the conductive filler in the polymer component, prepared for example in an internal batch mixer.

For example, the present invention can be used to modify a process of the type disclosed in International Patent Publication No. WO 98/05503. That process  
25 comprises making a conductive polymer laminate by  
(A) loading a dry blend of the polymeric component and the conductive filler into a mixing apparatus;  
(B) mixing the polymeric component and the conductive filler in the mixing apparatus to form a molten mixture;  
30 (C) transporting the molten mixture from the mixing apparatus through a die;  
(D) forming the molten mixture into a polymeric sheet; and  
(E) attaching metal foil to at least one side of the sheet to form a laminate,  
steps (A) to (E) being conducted sequentially in a single continuous procedure.

35 In the present invention, the molten conductive polymer must pass through the apparatus as a continuous stream, but the duration of the process can be short or long.

-6-

For example, when the conductive polymer is first prepared in an internal batch mixer and is then added as a molten mixture to the conveying means, the process may last for only a few minutes while the batch is processed.

5           Referring now to the drawing, this illustrates a single screw extruder 1, a passageway 2, a first gear pump 3, an extrusion head 4 having a nozzle orifice 41, and a second gear pump 5 having an exit 51. Pressure control system 8 monitors the pressure at junction of passageway 2 and first gear pump 3, and controls the operation of the second gear pump 5 in response to that pressure. Pellets of conductive polymer  
10 are fed from hopper 7 into extruder 1, which melts the conductive polymer and conveys it as a continuous stream under pressure through passageway 2 to the first gear pump 3. The first gear pump forces the molten conductive polymer through the extrusion orifice 41. The extrudate is calendered into a sheet by rollers 6. If the pressure observed by control system 8 exceeds a first preselected level, the control  
15 system switches on the second gear pump 5 so that molten conductive polymer is removed from the passageway 2 and discharged through exit 51. When the pressure observed by the control system 8 has dropped to a second selected level, it switches off the second gear pump 5.

20

-7-

CLAIMS

1. Apparatus for producing a melt-extruded article composed of a conductive polymer, the apparatus comprising
- 5 (1) conveying means for conveying a molten conductive polymer under pressure;
- (2) a passageway;
- (3) a first gear pump;
- (4) an extrusion orifice; and
- 10 (5) a polymer relief means
- the components (1), (2), (3) and (4) being arranged so that molten conductive polymer conveyed by the conveying means passes in a continuous stream sequentially through the conveying means, the passageway, the first gear pump and the extrusion orifice; and
- 15 the polymer relief means being associated with the first gear pump so that, if the pressure in the first gear pump exceeds a selected level, the polymer relief means removes molten conductive polymer from the continuous stream thereof until the pressure in the first gear pump falls below a second selected level.
- 20
2. Apparatus according to claim 1 wherein the polymer relief means is a second gear pump which, when it is operating, removes molten conductive polymer from the passageway.
- 25
3. Apparatus according to claim 2 wherein the ratio of the maximum capacity of the first gear pump to the maximum capacity of the second gear pump is 5:1 to 50:1.
4. Apparatus according to claim 2 or 3 wherein the conveying means comprises a single screw extruder or a twin screw extruder.
- 30
5. Apparatus according to claim 2 or 3 wherein the conveying means comprises a reciprocating single screw extruder.
6. Apparatus according to claim 2 or 3 wherein the conveying means is a non-
- 35 reciprocating screw extruder having an l/d ratio of 8:1 to 15:1.

-8-

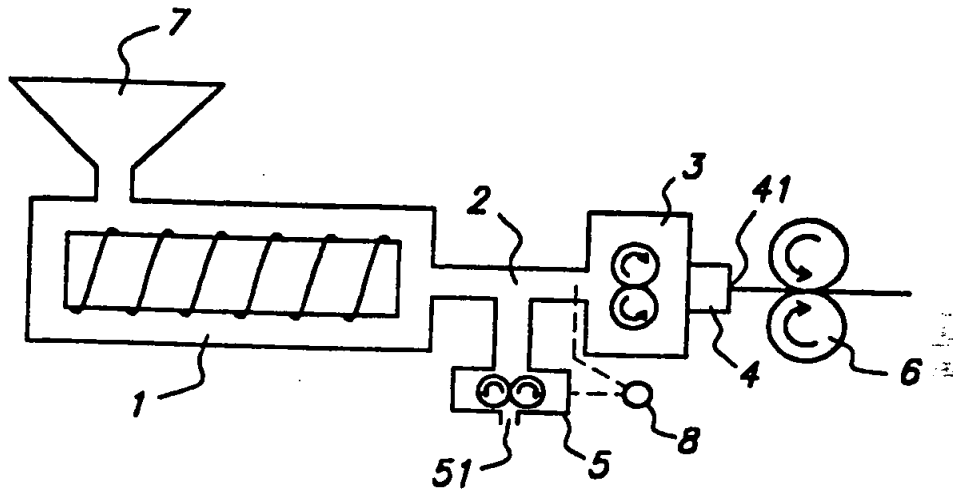
7. Apparatus according to any one of claims 2 to 6 wherein the extrusion orifice is a nozzle die.
8. Apparatus according to any one of claims 2 to 7 which includes a control system  
5 which continuously monitors the pressure exerted on the conductive polymer in the first gear pump and operates the second gear pump in response to that pressure.
9. A method of making an article composed of a conductive polymer, the method comprising the steps of
- 10 (A) conveying a continuous stream of a molten conductive polymer under pressure to a first gear pump;
- (B) operating the first gear pump so that the molten conductive polymer conveyed to the first gear pump in step (A) passes through the first gear pump to an extrusion orifice and is extruded through the orifice; and
- 15 (C) when the pressure within the first gear pump exceeds a selected level, removing molten conductive polymer from the continuous stream thereof.
10. A method according to claim 9 wherein in step (C) the molten conductive polymer is removed by means of a second gear pump.
- 20 11. A method according to claim 10 wherein the conductive polymer
- (i) comprises a polymer having a melting point  $T_m$  °C;
- (ii) has a viscosity of 2 to 15 K.Pa.sec at a shear rate of 50 sec<sup>-1</sup> and at a temperature of 1.5 times  $T_m$ ; and
- 25 (iii) is extruded at a temperature of not more than 1.5 times  $T_m$ .
12. A method according to claim 11 wherein the molten conductive polymer has a viscosity of 8 to 11 K.Pa.sec. at a shear rate of 50 sec<sup>-1</sup> and at a temperature of 1.5 times  $T_m$ .
- 30 13. A method according to any one of claims 10 to 12 wherein the conductive polymer contains at least 35% by volume of at least one particulate filler.
14. A method according to any one of claims 10 to 12 wherein the conductive  
35 polymer exhibits PTC behavior and contains at least 40% by volume of carbon black.

-9-

15. A method according to any one of claims 10 to 14 wherein the extrusion orifice is a nozzle die, and the extrudate is calendered into a sheet.
16. A method according to any one of claims 10 to 15 wherein the extrusion orifice  
5 is a sheet die having a gap of at most 0.13 mm (0.005 in).
17. A method according to claim 9 which is carried out using apparatus as claimed in any of claims 1 to 8.
- 10 18. A conductive polymer article prepared by a method as claimed in any of claims 9 to 17.

15

1/1



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/14159

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 B29C47/92 B29C47/50

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 078 513 A (R. LEVISON) 26 February 1963 see column 3, line 64 - column 4, line 3 see claim; figure 2	1,9
P, Y	W0 98 05503 A (RAYCHEM CORP) 12 February 1998 cited in the application see page 10, line 33 - page 11, line 11 see claims	1,9
A		2-8, 10-17
A	US 4 213 747 A (FRIEDRICH REINHARD) 22 July 1980 see figure 2	1-8
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

15 October 1998

Date of mailing of the international search report

22/10/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Jensen, K

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 98/14159

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 885 457 A (AU ANDREW N) 5 December 1989 see the whole document	1,9
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 189 (M-821), 8 May 1989 & JP 01 016422 A (ISUZU MOTORS LTD), 19 January 1989 see abstract	1-8

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 98/14159

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3078513	A	26-02-1963	FR 1114680 A	16-04-1956
			GB 774430 A	
			NL 95803 C	
			US 2867004 A	06-01-1959
WO 9805503	A	12-02-1998	AU 3742997 A	25-02-1998
US 4213747	A	22-07-1980	DE 2751225 A	17-05-1979
			FR 2409144 A	15-06-1979
			GB 2009972 A, B	20-06-1979
			JP 1429339 C	09-03-1988
			JP 54078762 A	23-06-1979
			JP 62034532 B	28-07-1987
US 4885457	A	05-12-1989	AT 109716 T	15-08-1994
			CA 1330698 A	19-07-1994
			DE 68917472 D	15-09-1994
			DE 68917472 T	20-04-1995
			EP 0436584 A	17-07-1991
			JP 4500938 T	20-02-1992
			WO 9003257 A	05-04-1990

